Gas Absorption with First-Order Reaction in Turbulent Liquid Films

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Under usual operating conditions for gas absorption the controlling mass transfer resistance resides in the liquid phase. In the work reported here, a previously proposed eddy diffusivity expression is used to analyze gas absorption accompanied by first-order chemical reaction in turbulent liquid films ($Re > 1200$). Asymptotic solutions to the diffusion equation are obtained for both short and long exposure times and for slow and fast reactions. These asymptotic solutions are used to obtain an interpolation formula which is valid over the complete range in parameters. The motivation for this work is that for many applications, such as liquid flow in packed columns, the contact times between complete mixing may not be sufficiently long to achieve fully developed conditions in the liquid. In this case information regarding the mass transfer coefficient at intermediate exposure times would be of interest.

Liquid phase mass transfer across a free surface has been treated in terms of an eddy diffusivity by Levich (1962), Davies (1966), and King (1966). Lamourelle and Sandall (1972) have experimentally determined the behavior of the liquid phase eddy diffusivity near the free surface from gas absorption measurements in a long wetted-wall column. These authors found that the eddy diffusivity varies as the square of the distance from the free surface.

$$\epsilon = ay^2 \tag{1}$$

For water at 25°C, a was found to be

$$a = 7.90 \times 10^{-5}\, Re^{1.678} \tag{2}$$

Equation (1) is valid for the region adjacent to the free surface. The major resistance to mass transfer occurs close to the free surface because of the large Schmidt numbers usually encountered in liquids, and thus it is important to know the eddy diffusivity accurately only in this region. Equation (1) has been used by Mills and Chung (1973) to correlate heat transfer rates across turbulent liquid films and by Menez and Sandall (1973) to describe gas absorption with first-order reaction at long exposure times.

The differential equation describing gas absorption accompanied by first-order irreversible reaction is

$$u(y)\frac{\partial c}{\partial x} = \frac{\partial}{\partial y}\left[(D + \epsilon(y))\frac{\partial c}{\partial y}\right] - k(c - c_e) \tag{3}$$

Equation (3) neglects axial transport and assumes no diffusion-induced velocity. The boundary conditions of interest are expressed as

$$\begin{aligned} &\text{(i)} \quad x = 0 \quad c = c_0 \\ &\text{(ii)} \quad y = 0 \quad c = c_s \\ &\text{(iii)} \quad y = d \quad \frac{\partial c}{\partial y} = 0 \end{aligned} \tag{4}$$

Two simplifying assumptions are made in solving Equations (3) and (4). It is assumed that the velocity u may be taken to be constant at its surface value. This assumption is made since the velocity gradient at the free surface vanishes for the case of no shear at the free surface and the turbulent film velocity profile will be relatively flat. It is further assumed that the eddy diffusivity given by Equation (1) for the surface region is valid over the complete film thickness. This assumption should not lead to any significant error since the major resistance to mass transfer lies near the free surface. With these assumptions Equations (3) and (4) may be written in dimensionless form as

$$\frac{\partial \bar{c}}{\partial x} = \frac{\partial}{\partial y}\left[(1 + \alpha\bar{y}^2)\frac{\partial \bar{c}}{\partial \bar{y}}\right] - \bar{c} \tag{5}$$

$$\begin{aligned} &\text{(i)} \quad \bar{x} = 0 \quad \bar{c} = \theta \\ &\text{(ii)} \quad \bar{y} = 0 \quad \bar{c} = 1 \\ &\text{(iii)} \quad \bar{y} = \gamma \quad \frac{\partial \bar{c}}{\partial \bar{y}} = 0 \end{aligned} \tag{6}$$

ASYMPTOTIC SOLUTIONS

For the limiting case of slow reactions we have $k \to 0$ or $\alpha \to \infty$, corresponding to physical absorption. Asymptotic solutions may be obtained for this case for both large and small values of $\bar{x}$. For large $\bar{x}$ and large α, corresponding to physical absorption in long films, Lamourelle and Sandall (1972) solve Equations (3) and (4) to obtain

$$\frac{Sh}{\gamma} = \frac{2}{\pi}\alpha^{1/2} \tag{7}$$

For physical absorption into short films the mass transfer coefficient is given by the penetration theory of Higbie (1935). Thus the large α, small $\bar{x}$ asymptote is given by

$$\frac{Sh}{\gamma} = \frac{1}{(\pi\bar{x})^{1/2}} \tag{8}$$

An asymptotic solution to Equations (5) and (6) may be obtained for the limiting case of fast reactions. As k becomes very large, $\alpha \to 0$ and the resulting equations have been solved by Lightfoot (1958) and by Astarita and Beek (1962) to give

$$\bar{c} = \frac{1}{2}\left[e^{\bar{y}}\, erfc\left(\frac{\bar{y}}{2\sqrt{x}} + \sqrt{\bar{x}}\right) + e^{-\bar{y}}\, erfc\left(\frac{\bar{y}}{2\sqrt{\bar{x}}} - \sqrt{\bar{x}}\right)\right] + \theta c^{-\bar{x}}\, erfc\,\frac{\bar{y}}{2\sqrt{\bar{x}}} \tag{9}$$

A correction term to Equation (9) can be obtained by a small parameter perturbation around $\alpha = 0$, but this does not significantly extend the range of applicability of Equation (9).

In the limit of large $\bar{x}$, the mass transfer coefficient obtained from Equation (9) is

$$\frac{Sh}{\gamma} = 1 \tag{10}$$

The small $\bar{x}$ asymptotic value of the mass transfer coefficient as determined from Equation (9) is

$$\frac{Sh}{\gamma} = \frac{e^{-\bar{x}}}{(\pi\bar{x})^{1/2}} \tag{11}$$

NUMERICAL SOLUTION

Equation (5) and (6) were solved numerically using finite differences approximations for the various derivatives. One difficulty encountered in the numerical solution was that a very fine increment size is required around $\bar{y} = 0$ because of the steep gradient in $\bar{c}$ in this region, whereas a relatively large increment size is sufficient as $\bar{y}$ approaches γ. This problem was overcome by scaling $\bar{y}$ according to the s-transformation proposed by Solbrig and Gidaspow (1968)

$$s = \int_0^{\bar{y}} \frac{d\bar{y}}{1 + \alpha\bar{y}^2} \Big/ \int_0^{\gamma} \frac{d\bar{y}}{1 + \alpha\bar{y}^2} \tag{12}$$

The Crank-Nicholson technique was used for the numerical solutions. The calculations were performed over a range in α from 0.1 to 100 for the inlet concentration θ taken to be zero. The other parameter which appears in the equations is the dimensionless film thickness γ. It was found that, as expected, the solution is not affected by a variation in γ. The reason for this is that the major resistance to mass transfer resides very near the free surface, and thus the position of the wall has little influence on the mass transfer.

The numerical results were combined with the asymptotic solutions using the technique of Churchill and Usagi (1972) to obtain a single empirical formula valid over the complete range in the parameters.

In our case the technique was applied twice, first taking α and then $\bar{x}$ as the independent variable. For large $\bar{x}$ the following were defined: $Y = Sh/\gamma$, $Z = 2/\pi\ \alpha^{1/2}$. A best fit to $Y = (1 + Z^n)^{1/n}$ was searched in terms of n. The integer value 2 was found to be satisfactory. This then gave

$$\frac{Sh}{\gamma} = \left(1 + \frac{4}{\pi^2}\alpha\right)^{1/2} \tag{13}$$

which interpolates the numerical results obtained for the fully developed Sherwood number to within a maximum deviation of 1.6%. No interpolation for the small $\bar{x}$ asymptotes was necessary since Equation (8) and (11) give equivalent results for $\bar{x} \to 0$. Thus Equation (13) for large $\bar{x}$ was combined with Equation (11) for small $\bar{x}$ by defining

$$Y = \frac{Sh/\gamma}{e^{-\bar{x}}/(\pi\bar{x})^{1/2}},\quad Z = \frac{\left(1 + \frac{4}{\pi^2}\alpha\right)^{1/2}}{e^{-\bar{x}}/(\pi\bar{x})^{1/2}}.$$

$n = 2$ was again found to satisfy $Y = (1 + Z^n)^{1/n}$ for intermediate $\bar{x}$ values, which then gave

$$\frac{Sh}{\gamma} = \left(1 + \frac{4\alpha}{\pi^2} + \frac{e^{-2\bar{x}}}{\pi\bar{x}}\right)^{1/2} \tag{14}$$

Figure 1 compares Equation (14) with the exact results. As can be seen, Equation (14) fits the numerical results well; the maximum deviation being 6.5%. Equation (14) is an empirical formula which is valid for any reaction rate from slow to fast and for any film length. The square root dependence of the Sherwood number on the asymptotic values in Equation (14) can be justified theoretically in an approximate way by application of the integral method to Equation (5) after applying the transformation given by Equation (12).

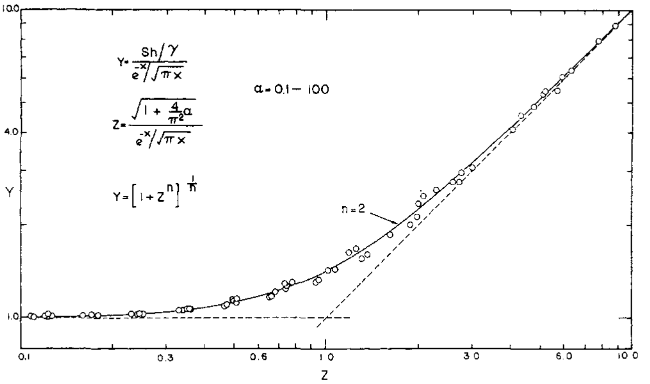

Fig. 1. Empirical correlation for gas absorption with first-order reaction.

ENHANCEMENT FACTOR

It is of interest to consider the ratio of the mass transfer coefficient with chemical reaction to the mass transfer coefficient without chemical reaction since this ratio may have a more general application than the mass transfer coefficient alone. Taking the limit of Equation (14) as $k \to 0$ for physical absorption and dividing the result into Equation (14) gives an equation for the enhancement factor.

$$\frac{k_c}{k_c^0} = \left[\frac{e^{-2\bar{x}} + \pi\bar{x}(1 + 4\alpha/\pi^2)}{1 + \frac{4\alpha\bar{x}}{\pi}}\right]^{1/2} \tag{15}$$

NOTATION

a = turbulence parameter in eddy diffusivity expression, 1/s

c = solute concentration in liquid, g moles/cm^3

$\bar{c}$ = dimensionless concentration $= \dfrac{c - c_e}{c_s - c_e}$

c_b = bulk solute concentration $= \int_0^d ucdy \Big/ \int_0^d udy$, g moles/cm^3

c_e = equilibrium solute concentration, g moles/cm^3

c_0 = inlet solute concentration, g moles/cm^3

c_s = solute concentration at gas-liquid interface, g moles/cm^3

d = film thickness, cm

D = molecular diffusion coefficient, cm^2/s

$erfc(x) = \dfrac{2}{\sqrt{\pi}}\int_x^\infty e^{-\lambda^2} d\lambda$

k = first-order reaction rate constant, 1/s

k_c = mass transfer coefficient $= -D\left(\dfrac{\partial c}{\partial y}\right)_{y=0} \Big/ (c_s - c_b)$, cm/s

k_c^0 = mass transfer coefficient for physical absorption, cm/s

Re = Reynolds number $= 4ud/\nu$

Sh = Sherwood number $= k_c d/D$

u = velocity, cm/s

x = distance parallel to interface, cm

$\bar{x}$ = dimensionless distance parallel to interface $= kx/u$

y = distance normal to interface, cm

$\bar{y}$ = dimensionless distance normal to interface $= \sqrt{\dfrac{k}{D}}\, y$

Greek Letters

α = dimensionless diffusion parameter = a/k
γ = dimensionless film thickness = $d(k/D)^{1/2}$
ϵ = eddy diffusion coefficient
θ = dimensionless inlet concentration = $\dfrac{c_0 - c_e}{c_s - c_e}$
ν = kinematic viscosity, cm^2/s

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Induction-Period Kinetics in Acrylamide Photopolymerization

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In a recent study of photopolymerization of acrylamide (Sandru and Smith, 1973) the induction period was observed to depend upon monomer concentration as well as light intensity and initiator concentration. This note reports the results of a careful quantitative study of the kinetics of the induction period during which dissolved oxygen in the aqueous solution is consumed. Of specific interest was the effect of monomer concentration.

Induction times were measured at 25°C, in the same batch-recycle photoreactor as employed by Sandru and Smith (1973), for aqueous solutions of various concentrations of monomer (0.05 to 0.5 g mole/liter), initiator (1×10^{-3} to 6.5×10^{-3} g mole/liter of potassium persulfate) and dissolved oxygen. Since the polymer of acrylamide is insoluble in methanol, the induction time was determined by noting the onset of turbidity with a Hach turbidimeter, when a 4-cm^3 sample of the reaction mixture was added to 10-cm^3 of methanol. Induction times, and hence rates of reaction were reproducible within 4%. The annular reactor had an inside radius of 33.5 mm and an outer radius of 45 mm and an irradiated length of 8.2 cm. Radiation was from a high-pressure mercury lamp (Hanovia 679A-36, 450 watts) placed at the axis of the annulus. There was significant radiation from this lamp in the range 2224 to 4358 Å. The volumes of reactor and reservoir and the circulation rate of the recycle system were such that the reactor operated at close to differential conditions as long as the conversion of oxygen (the limiting reactant) per pass was less than 20%. That is, the error in assuming a constant rate through the reactor was less than 10% if conversions per pass of oxygen were 20% or less. Complete descriptions of these factors and the apparatus are available (Ibarra, 1973).

Different initial oxygen concentrations were obtained by varying the severity of stripping of the solution with helium. Initial concentrations ranged from about 0.2×10^{-4} to 2.4×10^{-4} g mole/liter and were measured by the Winkler optical method (Procedures Manual, Delta Scientific Company, 1968). In all runs the oxygen concentration was less than one-tenth of that of initiator.

Light intensity was varied by circulating a solution of $\mathrm{Fe\,Cl_3 \cdot 6\,H_2O}$ and HCl, of different concentrations, through an annular jacket between the reactor and the lamp. Such filter solutions absorb about the same fraction of radiation regardless of the wave length so that the spectral distribution of the light reaching the reactor remains approximately the same. A Corex filter directly adjacent to the lamp also was employed to reduce the level of intensity. This was necessary because preliminary experiments with a higher intensity lamp (Hanovia LL 189A, 1200 watts) resulted in formation of a film of insoluble (in water and common solvents) polymer on the inner-wall surface of the reactor. The Corex filter transmitted no radiation at wave lengths shorter than 2482 Å and the absorptivities of initiator and monomer were negligible beyond 3660 Å. Hence, the effective range of radiation was from 2482 to 3660 Å.

The total light intensity $I_{b,t}$ at the inside wall surface of the reactor was determined using the uranyl oxalate actinometer (Sandru and Smith, 1973). Results for $I_{b,t}$ as a function of lamp operating time are shown in Table 1. Since the final induction runs were made after the second